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Pulsed laser deposition of silicon containing carbon thin films

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Abstract

Amorphous, hydrogenated carbon thin films with varying silicon content (a-$Si_{(1-x)}C_x$:H) for optical and tribological applications were deposited by means of pulsed laser deposition (PLD) from silicon targets with a high power pulsed Nd:YAG laser of 1064-nm wavelength in argon and C_2H_2 containing atmospheres. To minimize the deposition of particulates and droplets originating in the laser ablation process of the pure silicon targets, a perpendicular arrangement of the target and substrate surface as well as a screen between them was applied ('shaded off-axis' geometry). The chemical composition was investigated employing X-ray photoelectron spectroscopy, revealing carbon contents between 80 and 97 at.% and a mainly C–C_4 bonded structure. A distinct effect of the carbon content on the hardness and elastic modulus of the films determined by nanoindentation was observed. In contrast, the optical behavior of the films investigated employing spectroscopic ellipsometry was found to be nearly independent on the carbon content. A comparison of the optical properties for all films with literature data revealed a hydrogenated diamond-like carbon bonding structure.

Keywords: Carbon; Silicon carbide; Spectroscopic ellipsometry; Pulsed laser deposition (PLD); Laser ablation; Shaded off-axis

1. Introduction

Materials in the silicon–carbon system possess a great variety of interesting physical, electrical and optical properties, such as high hardness values and low friction coefficients, wide bandgap, high thermal conductivity, good resistance to chemical attack and nearly wavelength independent refractive indices. Thus, these materials are promising materials for high-temperature, high-power and high-frequency electronic devices [1], as well as for optoelectronic devices [2,3] and protective layers for solar cells [4]. However, the knowledge of the properties of non-stoichiometric hydrogenated amorphous carbon–silicon compounds ($Si_{(1-x)}C_x$:H) is very limited due to the difficulties of amorphous film deposition with most of the CVD and PVD techniques. The pulsed laser deposition (PLD) is a suitable method for the deposition of amorphous thin $Si_{(1-x)}C_x$:H films at low temperatures with high adhesion to the substrate material [5–9]. The technique is based on the removal (ablation) of material from a target by a focused high-energy laser beam. The interaction of the laser beam with the target produces a highly orientated material stream, consisting of neutral and ionized atomic or molecular high energetic species. Besides atomic and molecular species, some micron and submicron sized particles and droplets are ejected as well from the target and incorporated in the films. This phenomenon depends on many factors such as roughening of the target surface during the ablation process, the fluence and wavelength of the laser, the density of the target and the chemical and physical properties of the target material [10,11]. The incorporation of these particulates in the growing films causes the presence of structurally inhomogeneous bulk regions and an increased surface roughness, which are not acceptable in a large number of technological applications. One approach to minimize the droplet deposition is the modification of the deposition conditions, using the 'shaded off-axis' technique [11,12]. In

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Table 1
Deposition parameters and chemical composition of the amorphous PLD $Si_{(1-x)}C_x$:H films.

Film	Gas flow (sccm)		Deposition rate (10^{-3} nm/pulse)	Film thickness (nm)	Chemical composition (at.%)			x in $Si_{(1-x)}C_x$:H
	C_2H_2	Ar			Si	C	O	
SiC 1	5	25	8.9	320	18.6	72.6	8.8	0.80
SiC 2	15	15	8.7	313	7.2	89.7	3.1	0.93
SiC 3	30	0	9.5	342	2.8	95.8	1.4	0.97
SiC 4	45	0	15.4	554	3.2	95.3	1.5	0.97

this arrangement, the irradiated target and the substrate surfaces are placed perpendicular to each other in the deposition chamber. Furthermore, a metallic screen is placed between them for screening off the droplets from the substrate's surface. For the deposition of SiO_x thin films ($0=x=2$) it was found that a reduction of the droplet covered area on the coated substrates up to a factor of 100 compared to a parallel arrangement of substrate and target is possible by applying the shaded off-axis technique [11].

The aim of the present work is the application of the 'shaded off-axis' PLD technique in the deposition of non-stoichiometric $Si_{(1-x)}C_x$:H thin films. To achieve very high carbon contents in the films, acetylene was used for the reactive deposition of $Si_{(1-x)}C_x$:H thin films by ablation of a silicon target with a 1064 nm Nd:YAG laser beam. The chemical, mechanical and optical properties were characterized and indicate a distinct dependency on the carbon content.

2. Experimental

2.1. Film deposition

High purity silicon targets (99.95% Si) were used for the ablation experiments with a pulsed Nd:YAG laser, which provides a beam with 1064-nm wavelength, 0.8 J pulse energy and 10 ns pulse duration at a repetition rate of 10 Hz [13]. The targets were rotated during the laser irradiation in order to avoid the formation of deep craters. The emitted species were deposited at room temperature (approx. 298 K) onto single crystalline (100) orientated silicon substrates mounted perpendicular to the irradiated target surface behind a screen of 1-cm height ('shaded off-axis' technique) [11]. Prior to deposition, the substrates have been cleaned ultrasonically in pure acetone and subsequently in pure ethanol to avoid a contamination of the growing films. The reaction chamber was evacuated before starting the deposition process to pressures below 2×10^{-3} Pa by a pumping unit consisting of an oil diffusion and a rotary pump. The process gas flow (Ar, C_2H_2), which is necessary for scattering of the ablated species behind the screen in order to reach the substrate surface as well as for the reactive deposition was adjusted by means of electronic mass flow controllers.

2.2. Film characterization

The surface quality of the films was inspected with light microscopy. The film structure was investigated by grazing incidence X-ray diffraction (XRD) using a Bruker AXS D8 Discover. The characterization of the chemical composition and the chemical bonding of the films was performed by X-ray photoelectron spectroscopy (XPS) using an Omicron Multiprobe system with a monchromized AlKα (1486.6 eV) X-ray beam and a resolution of the analyzer better than 0.3 eV [11]. The detection sensitivity of this equipment was approximately 1 mass%.

The mechanical properties—hardness and Young's modulus of the films were measured by nanoindentation with a cube corner indenter. The applied maximum loads were approximately 220 μN, the loading rates 20 nm s^{-1} for all measurements on the Hysitron Triboscope® facility of the Nanoscope III® (Digital Instruments Inc.) equipment.

The optical properties of the films were determined using a variable angle spectroscopic ellipsometer (J.W. Woollam Comp. Inc.) at angles of incidence between 65 and 85° in the spectral range from 340 to 1100 nm with 2 nm spectral resolution. The fitting of the measurement data for the calculation of the refractive indices and extinction coefficients as well as for the film thicknesses was performed using the Cauchy dispersion [14] and the Urbach relation [15], respectively.

3. Results and discussion

The results in Table 1 show that the use of different gas mixtures for the deposition of the $Si_{(1-x)}C_x$:H films strongly influences the deposition rate. Due to the high reactivity of the acetylene in the ablated plasma cone, a drastic increase of the deposition rate at higher C_2H_2 gas flows was found especially for the film 'SiC 4', which can be attributed to the approximately 40% higher total pressure compared to the other films. In contrast, the particulate (droplet) density on the film surfaces, investigated by light microscopy drops down from

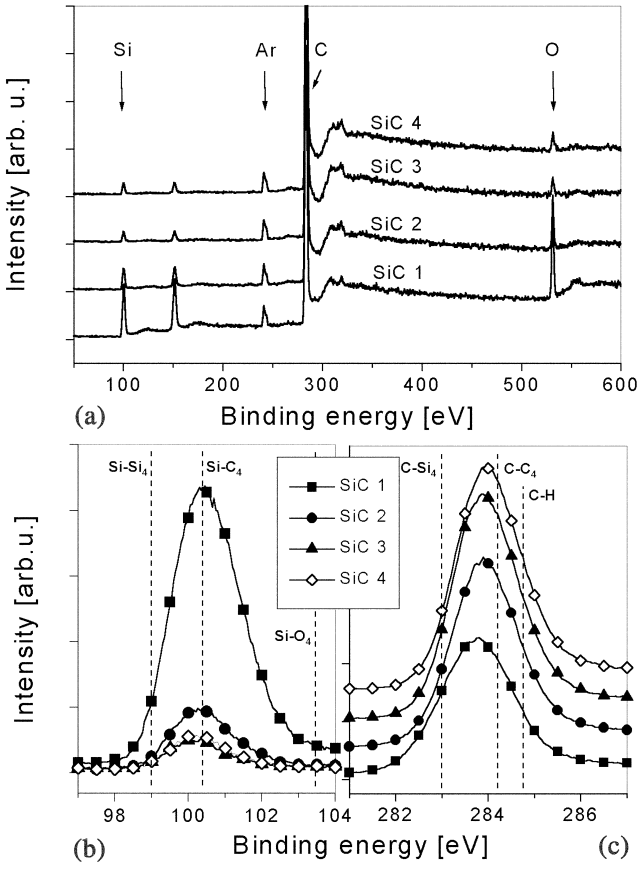

Fig. 1. XPS spectra taken from the film after 30 min Ar sputtering: (a) energy range from 50 to 600 eV to show all detected elements; (b) energy range from 97 to 104 eV to show the silicon excitation states; and (c) energy range from 283 to 287 eV to show the carbon excitation states.

approximately 3.1×10^3 cm^{-2} ('SiC 1') to 1.5×10^3 cm^{-2} ('SiC 4') at higher C_2H_2 gas flows. The ratio of particulate density/film thicknesses (see Table 1) was found to be nearly constant. XRD investigations with grazing incidence (0.5, 1.5 and 3°) of the primary beam revealed a fully amorphous structure of all films investigated.

XPS measurements have been performed for determining the film composition as well as the chemical bonding after sputtering the film surface with an Ar^+ ion beam for 30 min to exclude the influence of film contamination during sample handling in air. As shown in Fig. 1a, the films are contaminated with oxygen and argon, the latter element is mainly incorporated by sputtering prior the XPS measurement. This can be seen by comparing the spectra of the films 'SiC 1' and 'SiC 2', deposited in C_2H_2+Ar atmospheres, with 'SiC 3' and 'SiC 4', grown in pure C_2H_2 atmosphere. In all spectra, the argon peak shows nearly the same intensity. The oxygen contamination is caused by the remaining gas in the recipient after evacuation as well as from the technically clean ethylene gas used as reactive gas. The oxygen content determined from the O peak areas was found to be up to approximately 9 at.%. In spite of the relatively high oxygen contamination, the Si2p signal consists only of one peak centered at 100.4 eV for all films (Fig. 1b), which is expected for SiC [16]. No signal intensity could be observed at the position of SiO_2 ($Si-O_4$) approximately 103.5 eV [17]. In contrast, the position of the C1s peak (Fig. 1c) is influenced by the deposition conditions. The higher the C_2H_2 gas flow, the larger is the shift to higher binding energies. This shift can be attributed to the decreasing content of carbide-type bonded carbon ($C-Si_4$ at 283.0 eV) and the increasing content of graphite-type bonded carbon ($C-C_4$ at 284.2 eV) [18,19] at higher C_2H_2 gas flows. Furthermore, the C1s peaks of all films are assymetrical, revealing the presence of an additional contribution around a binding energy of 284.8 eV, which originates from the C–H bonds in the $Si_{(1-x)}C_x$:H films [17].

The chemical compositions determined from the XPS measurements are shown in Table 1. The carbon content (x) in the $Si_{(1-x)}C_x$:H films was found between 0.80 and 0.97—the highest carbon contents were found in the films deposited at the highest C_2H_2 flows. In the shaded off-axis deposition technique, relatively high process gas pressures are necessary in order to enable an intensive scattering of the ablated species. This scattering is the prerequisite for a film growth at the substrate surface behind the metallic screen. Thus, a higher content of C_2H_2 molecules in the recipient leads to a higher probability of scattering [12], resulting in intensive dissociation of C_2H_2 and an increased ionization of carbon and hydrogen. This causes higher deposition rates of carbon.

The chemical composition of the coatings influences significantly the mechanical properties as shown in Fig. 2. An increase of the carbon content leads to a nearly linear decrease of the hardness H and the reduced elastic modulus E (see Fig. 2). This tendency is in contrast to the results of Papakonstantinou et al. [20], who found

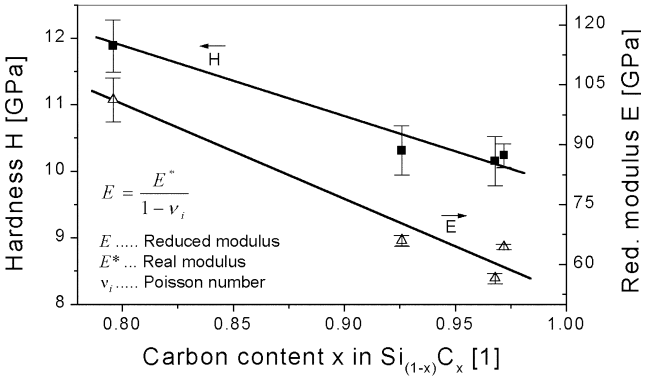

Fig. 2. Dependency of the hardness H and the reduced elastic modulus E on the chemical composition of the amorphous PLD $Si_{(1-x)}C_x$:H films.

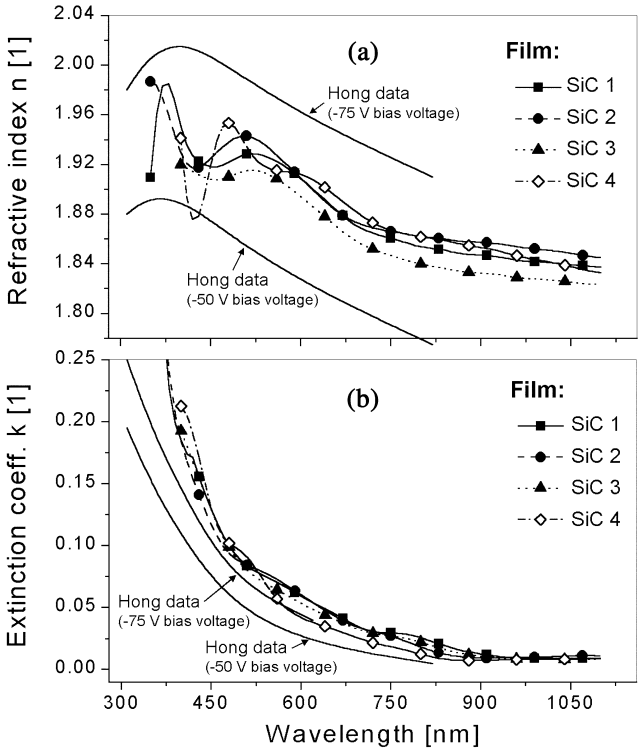

Fig. 3. Spectral variations of (a) refractive indices n and (b) extinction coefficients k of the amorphous PLD $Si_{(1-x)}C_x$:H films compared with Hong's data of a-C:H films [25].

for Si-containing diamond-like carbon (Si-a-C:H) films, a decrease of both mechanical properties with increasing silicon content. The hardness level of the PLD coatings is comparable to amorphous SiC:H films, obtained by reactive evaporation processes at temperatures between 573 and 773 K [21], but it is significantly lower than for Si-a-C:H films [20].

Although the chemical composition is changing in a wide range, the optical properties—refractive index n and extinction coefficient k—of the films are scarcely influenced by the carbon content (see Fig. 3). Over the whole spectral range investigated, nearly constant refractive indexes between 1.8 and 2.0 are found (Fig. 3a), which are very low compared to a-SiC:H ($n \sim 2.2$–2.5) [22,23] or crystalline SiC ($n \sim 3.4$) [24]. However, a good coincidence with a-C:H films that were sputtered at low temperatures and low bias voltages (between -50 and -75 V) can be observed in the spectral dependency and the position of the maximum (approx. 300–500 nm) of the refractive index (Fig. 3a) [4,25,26]. Besides the refractive index, the coefficient of extinction follows the same spectral dependency as the a-C:H films (Fig. 3b). Due to the similarity of the results of the optical investigations, the structure of our $Si_{(1-x)}C_x$:H films seems to be similar to the a-C:H film structure suggested by Robertson et al. [27] and Hong et al. [26]. This structure model describes a coexistence of sp^2 carbon bonded clusters in an sp^3 bonded network. The position of the (local) maximum of the refractive index at rather low wavelengths refers to a high amount of sp^2 bonds and thus, to low kinetic energies of the deposited particles, according to earlier results of silicon and silver based PLD films deposited in the 'shaded off-axis' technique [11,12].

4. Conclusions

Nearly droplet free hydrogenated silicon containing amorphous carbon ($Si_{(1-x)}C_x$:H) thin films were deposited onto shaded off-axis placed silicon substrates by pulsed laser ablation of silicon targets in C_2H_2 and Ar containing atmospheres. Strong influences of the C_2H_2 partial pressure during deposition on the growth rate (8.7–15.4×10^{-3} nm/pulse) and on the chemical and mechanical properties of the thin films were found. An increase of the C_2H_2 pressure leads to a significant increase of the carbon content from 80 to 97%, determined by a quantitative XPS analysis, resulting in higher contents of C–C_4 bonding in the films. As a result of this, the hardness and the reduced elastic modulus decrease nearly linear with increasing carbon content. The level of the hardness and the reduced elastic modulus is comparable to amorphous, C-rich films in the silicon–carbon system. The amorphous structure is obviously caused by the low kinetic energy of the deposited atoms and ions in the shaded off-axis technique and the presence of hydrogen in the films. The optical properties of all films are comparable to hydrogenated diamond-like carbon films (a-C:H), revealing a nearly similar amorphous structure to these thin films.

Acknowledgments

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